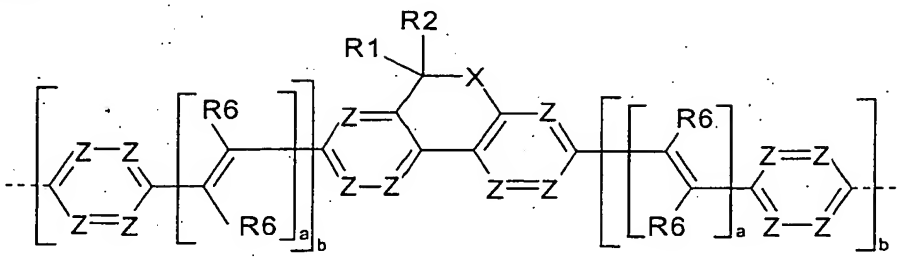
Claims:

1. A polymer, characterized in that it comprises at least 1 mol% of units of the formula (I),



FORMULA (I)

where the symbols and indices used have the following meanings:

X is identical or different on each occurrence and is in each case C(R3)(R4) or N(R3);

Z is identical or different on each occurrence and is in each case C(R5) or N;

R1, R2, R3, R4 are identical or different on each occurrence and are in each case H, fluorine, chlorine, bromine, iodine, CN, $N(R6)_2$, $Si(R6)_3$ or $B(R6)_2$, a straight-chain, branched or cyclic alkyl or alkoxy chain having from 1 to 22 carbon atoms in which one or more nonadjacent carbon atoms may also be replaced by NR6, O, S, O-CO-O, CONR6, $Si(R6)_2$, where one or more H atoms may also be replaced by fluorine, an aryl, heteroaryl or aryloxy group having from 5 to 40 carbon atoms in which one or more carbon atoms may also be replaced by O, S or N and which may also be substituted by one or more nonaromatic radicals R1, with two or more of the radicals R1 to R4 also being able to be joined to form a ring system; with the proviso that two substituents on one carbon atom are not at the same time an alkoxy or aryloxy side chain and that all substituents R1 to R4 are not at the same time H or not at the same time a methyl group;

R5 is identical or different on each occurrence and is in each case H, F, CN, $N(R6)_2$ or $B(R6)_2$, a straight-chain, branched or cyclic alkyl or alkoxy chain having from 1 to 22 carbon atoms in which one or more nonadjacent carbon atoms may also be replaced by O, S, CO-O, O-CO-O, CONR6, $Si(R6)_2$, where one or more H atoms may also be replaced by fluorine, an aryl, heteroaryl or aryloxy group having from 5 to 40 carbon atoms in which one or more carbon atoms may also be replaced by O, S or N and which may also be substituted by one or more nonaromatic radicals R5; with a plurality of radicals R5 or R5 together with R1 to R4 also being able to form a ring system;

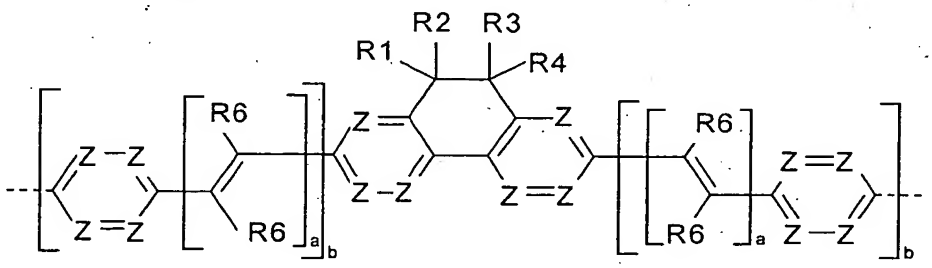
R6 is identical or different on each occurrence and is in each case H, a straight-chain, branched or cyclic alkyl chain having from 1 to 22 carbon atoms in which one or more nonadjacent carbon atoms may also be replaced by O, S, CO-O, O-CO-O, where one or more H atoms may also be replaced by fluorine, an aryl group having from 5 to 40 carbon atoms in which one or more carbon atoms may also be replaced by O, S or N and which may also be substituted by one or more nonaromatic radicals R6;

a is identical or different on each occurrence and is in each case 0 or 1;

b is identical or different on each occurrence and is in each case 0, 1 or 2;

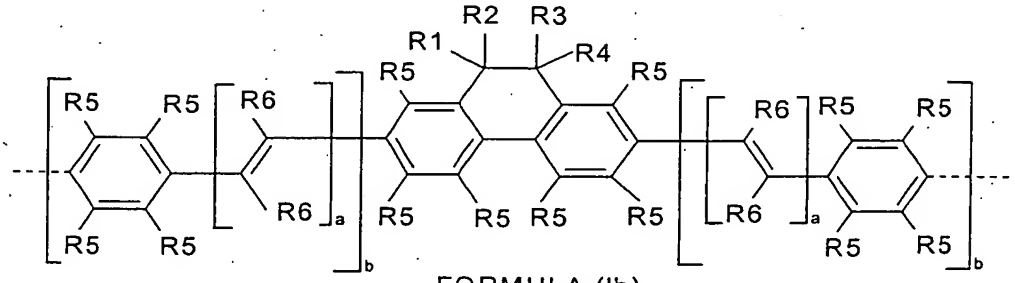
with the proviso that poly(arylene-vinylene) compounds in which one arylene unit is a 9,10-dialkyl-9,10-dihydrophenanthrene are excluded from the invention; the bond shown as a broken line indicates the linkage in the polymer.

2. The polymer as claimed in claim 1, characterized in that X is C(R3)(R4), as shown in formula (Ia):



FORMULA (Ia)

3. The polymer as claimed in claim 2, characterized in that Z is C(R5), as shown in formula (Ib):



FORMULA (Ib)

4. The polymer as claimed in one or more of claims 1 to 3, characterized in that it is conjugated.

5. The polymer as claimed in one or more of claims 1 to 4, characterized in that it further comprises additional units which significantly improve the hole injection and/or transport properties.

6. The polymer as claimed in claim 5, characterized in that the units having hole transport properties are selected from among the structural elements triarylamine derivatives, benzidine derivatives, tetraarylene-para-phenylenediamine derivatives, phenothiazine derivatives, phenoxazine derivatives, dihydrophenazine derivatives, thianthrene derivatives, dibenzo-*p*-dioxin derivatives, phenoxathiine derivatives, carbazole derivatives, azulene derivatives, thiophene derivatives, pyrrole derivatives, furan derivatives and further O-, S- or N-containing heterocycles having a high HOMO.

7. The polymer as claimed in one or more of claims 1 to 6, characterized in that it further comprises additional units which significantly improve the electron injection and/or transport properties.

8. The polymer as claimed in claim 7, characterized in that the units having electron transport properties are selected from the structural elements pyridine derivatives, pyrimidine derivatives, pyridazine derivatives, pyrazine derivatives, anthracene derivatives, triarylboranes, oxadiazole derivatives, quinoline derivatives, quinoxaline derivatives, phenazine derivatives, arylboranes and further O-, S- or N-containing heterocycles having a low LUMO.

9. The polymer as claimed in one or more of claims 1 to 8, characterized in that it comprises units which comprise combinations of individual units as claimed in claims 5 and 7.

10. The polymer as claimed in one or more of claims 1 to 9, characterized in that it comprises units which alter the emission characteristics so that electrophosphorescence can be obtained instead of electrofluorescence.

11. The polymer as claimed in claim 10, characterized in that the units which make a transfer from singlet excitons to triplet excitons possible and emit light with high efficiency from the triplet state even at room temperature are selected from among compounds which comprise heavy atoms having an atomic number of more than 36.

12. The polymer as claimed in claim 11, characterized in that the heavy atoms are selected from among the elements of groups 8 to 10 (i.e. Ru, Os, Rh, Ir, Pd, Pt).

13. The polymer as claimed in one or more of claims 1 to 12, characterized in that it comprises additional units which aid the transition from the singlet state to the triplet state.

14. The polymer as claimed in claim 13, characterized in that the structural units which aid the transition from the singlet state to the triplet state are selected from the group consisting of carbazoles and bridged carbazole dimers.

15. The polymer as claimed in one or more of claims 1 to 14, characterized in that further units which influence the morphology or the emission color of the resulting polymer and are selected from among aromatic structures having from 6 to 40 carbon atoms and stilbene, bisstyrylarylene and tolane derivatives, which may each be substituted by one or more nonaromatic radicals R1, are used.

16. The polymer as claimed in claim 15, characterized in that the structural elements described are selected from among 1,4-phenylene, 1,4-naphthylene, 1,4- or 9,10-anthracenylene, 1,6- or 2,7- or 4,9-pyrenylene, 3,9- or 3,10-perylenylene, 2,7- or 3,6-phenanthrenylene, 4,4'-biphenylylene, 4,4"-terphenylylene, 4,4'-bi-1,1'-naphthylylene, 4,5-dihydropyrene, 4,5,9,10-tetrahydropyrene, fluorene, spirobifluorene, 5,7-dihydrodibenzooxepin, cis- or trans-indenofluorene, 4,4'-stilbene, 4,4"-bisstyrylarylene and 4,4'-tolane derivatives.

17. The polymer as claimed in one or more of claims 1 to 16, characterized in that an average of at least 2 nonaromatic carbon atoms are present in the substituents per repeating unit.

18. The polymer as claimed in one or more of claims 1 to 17, characterized in that no long-chain substituents having more than 12 carbon atoms in a linear chain are present.

19. The polymer as claimed in one or more of claims 1 to 18, characterized in that the following applies to the symbols in the formula (I):

X	is C(R3)(R4) on each occurrence;
Z	is CH on each occurrence;
R1, R3	are identical or different on each occurrence and are each a straight-chain or branched alkyl chain having from 1 to 8 carbon atoms or an

aryl group having from 5 to 10 carbon atoms, in which one or more carbon atoms may also be replaced by N, S and/or O and which may also be substituted by one or more nonaromatic radicals R5;

R2, R4 are identical or different on each occurrence and are each a straight-chain or branched alkoxy chain having from 1 to 8 carbon atoms;

a is 1 on each occurrence if the units of the formula (I) are used as emitters;

b is 1 on each occurrence if the units of the formula (I) are used as emitters and is otherwise 0 on each occurrence;

and the other symbols are as defined in claim 1.

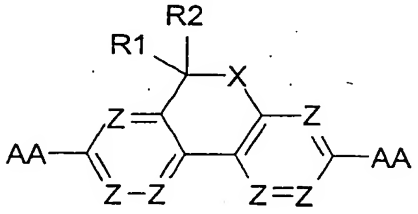
20. The polymer as claimed in one or more of claims 1 to 19, characterized in that the structural units of the formula (I) are selected from among units of the formulae (LXXIV) to (CVI).

21. The polymer as claimed in one or more of claims 1 to 20, characterized in that it comprises at least 40 mol% of units of the formula (I).

22. A blend (mixture) comprising one or more polymers as claimed in one or more of claims 1 to 21.

23. A solution comprising one or more polymers or blends as claimed in one or more of claims 1 to 22 in one or more solvents.

24. A monomeric bifunctional compound of the formula (CVII),



FORMULA (CVII)

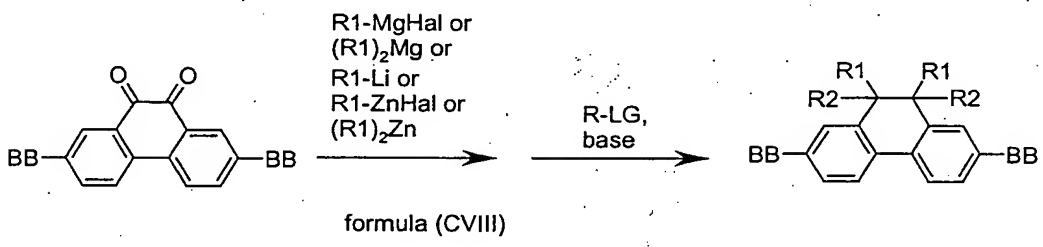
characterized in that the two functional groups AA, which may be identical or different, copolymerize under conditions of C-C coupling and the symbols X, Z and R1 to R6 have the same meanings as described in claim 1 with the proviso that not all radicals R1 to R4 can at the same time be fluorine or chlorine.

25. The compound as claimed in claim 24, characterized in that AA is selected from among the groups Cl, Br, I, O-tosylate, O-triflate, O-SO_2R5, $B(OH)_2$, $B(OR5)_2$ and $Sn(R5)_3$, where R5 is as defined in claim 1.

26. The compound as claimed in claim 24 and/or 25, characterized in that the C-C coupling reactions are selected from among SUZUKI coupling, YAMAMOTO coupling and STILLE coupling.

27. The compound as claimed in one or more of claims 24 to 26, characterized in that the monomeric compounds of the formula (CVII) lead to structural units of the formulae (LXXIX) to (CVI) in the polymer.

28. A process as shown in formula (CVIII) for preparing symmetrical, monomeric bifunctional compounds of the formula (CVII) in which X is C(R1)(R2) and Z is C(R5), characterized in that a phenanthrenequinone is reacted with an organomagnesium or organolithium or organozinc compound, followed by reaction with an alkylating reagent R-LG under basic conditions:



formula (CVIII)

where the symbols used have the following meanings:

BB is identical or different on each occurrence and is in each case H or has the same meaning as described for AA under claim 25;

R-LG is identical or different on each occurrence and is in each case an alkylating reagent, where R is an alkyl group and LG is a group which reacts as a leaving group under the conditions of nucleophilic aliphatic substitution, preferably Cl, Br, I, O-tosylate or O-triflate;

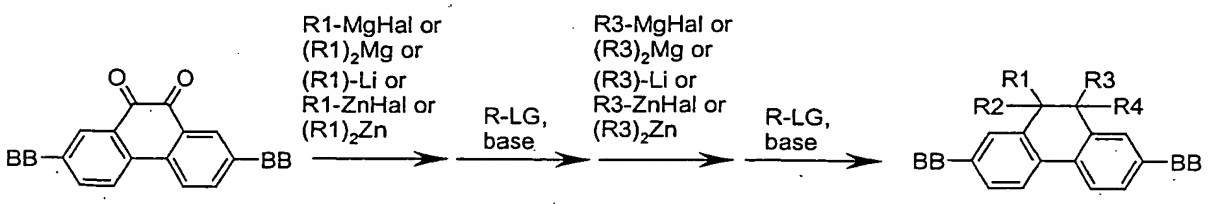
R1 is an alkyl, aryl or heteroaryl group;

R2 is an alkoxy group O-R, where R is as defined above;

Hal is F, Cl, Br, I.

29. A process as shown in formula (CIX) for preparing unsymmetrical, monomeric bifunctional compounds of the formula (CVII) in which X is C(R3)(R4) and Z is C(R5), characterized in that a phenanthrenequinone is reacted with an

organomagnesium or organolithium or organozinc compound, followed by reaction with an alkylating reagent R-LG under basic conditions and repetition of this reaction sequence:



formula (CIX)

where the symbols used have the following meanings:

BB is identical or different on each occurrence and is in each case H or has the same meaning as described above for AA;

R-LG is identical or different on each occurrence and is in each case an alkylating reagent, where R is an alkyl group, preferably a linear or branched alkyl chain having from 1 to 8 carbon atoms, and LG is a group which reacts as a leaving group under the conditions of nucleophilic aliphatic substitution;

R1, R3 are each an alkyl, aryl or heteroaryl group;

R2, R4 are each an alkoxy group O-R, where R is as defined above;

Hal is F, Cl, Br, I.

30. The process as claimed in claim 28 and/or 29, characterized in that the leaving group LG is Cl, Br, I, O-tosylate or O-triflate.

31. The process as claimed in one or more of claims 28 to 30, characterized in that a metal hydride, an alkoxide or a carbonate is used as base.

32. The process as claimed in one or more of claims 28 to 31, characterized in that a Grignard reagent is used as organometallic compound.

33. The use of a polymer as claimed in one or more of claims 1 to 22 in organic electronic devices.

34. The use of a polymer as claimed in one or more of claims 1 to 22 as electroluminescence material.

35. An organic electronic device comprising one or more active layers, wherein at least one of these active layers comprises one or more polymers as claimed in one or more of claims 1 to 22.

36. The organic electronic device as claimed in claim 35, characterized in that it is a polymeric light-emitting diode (PLED), an organic integrated circuit (O-IC), an organic field effect transistor (OFET), an organic thin film transistor (OTFT), an organic solar cell (O-SC), an organic photoreceptor or an organic laser diode (O-laser).

Abstract

Conjugated polymers, their preparation and use

The present invention relates to conjugated polymers which comprise novel structural units of the formula (I). The materials of the invention display improved efficiency and a longer life when used in polymeric organic light-emitting diodes.